THEORETICAL STUDIES OF IMPORTANT PROCESSES IN PLANETARY AND COMET ATMOSPHERES

Final Report

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A. Progress Under NASA Grants NAGW 1404 and NAG5-4316

Using theoretical quantum chemical calculations, I have successfully described the dissociative recombination (DR) of O_2^+ leading to the excited ^1S state of atomic oxygen, the upper state of the well known green line emission. The process is described by

$$O_2^+ + e^- \rightarrow O(^1S) + O(^1D) \qquad (1)$$

where e^- is an electron and the product oxygen atoms are both excited. This process is important in the atmospheres of Venus, Mars and Earth. I have shown in prior calculations [Guberman, 1987, 1988] that only one repulsive potential curve of O_2, $f^1\Sigma_u^+$, can generate $O(^1S)$ from DR of the lowest vibrational levels of O_2^+. However, in the prior results, the calculated quantum yield (i.e. the number of $O(^1S)$ atoms produced for every two product atoms) from the O_2^+ v=0 level was smaller than the laboratory and atmospheric measurements by more than an order of magnitude. Including only direct recombination, the calculated quantum yield for $O(^1S)$ is only 0.0016 [Guberman, 1987, 1988]. In a calculation [Guberman and Giusti-Suzor, 1991] that accounts for both direct and indirect recombination, the quantum yield is 0.0012. The range of experimentally determined quantum yields is between 0.01 and 0.23. Because of this large difference between the theoretical and experimental quantum yields, it was thought for some time that the ionospheric and laboratory O_2^+ must be vibrationally excited since for excited levels, theory gave quantum yields that are similar to experimental yields. It was also suggested that some other process was generating $O(^1S)$ but none could be identified [Bates, 1992].

Under current NASA support, I have found that reaction (1) proceeds via an unusual mechanism. The $f^1\Sigma_u^+$ state does not cross the ion between the turning points of the v=0 level of the O_2^+ ground state. The lack of a favorable crossing leads to a very small calculated DR rate coefficient. However, this mechanism assumes that initial electron capture must occur into the repulsive state that leads to $O(^1S)$. Instead, I have found that initial electron capture occurs mostly into the $B^3\Sigma_u^-$ state which crosses the ion between the turning points of the v=0 ion level and has a large DR rate coefficient. The B state dissociates to $O(^1D)$ and $O(^3P)$. After capture, some of the flux is transferred to the $f^1\Sigma_u^+$ state via symmetry mixed intermediate Rydberg states. The neutral Rydberg states are a mixture of $^1\Sigma_u^+$ and $^3\Sigma_u^-$ symmetry. The mixing is due to spin-orbit

coupling which splits the ground state of O_2^+ into two states separated by only 200cm^{-1}. Two mixed symmetry Rydberg series are involved. The lower Rydberg series limit is at the v=0 level of the $X^2\Pi_{1/2g}$ state and the other limit is 0.025eV higher at the v=0 level of the $X^2\Pi_{3/2g}$ state.

In order to do these calculation, the multichannel quantum defect computer code that is used for the calculation of DR cross sections and rates was extensively revised to handle the spin-orbit coupling. The calculations also make use of an earlier revision to handle ion core excited states since the upper spin-orbit level is a core excited state. The resulting cross section is shown in Figure 1. The region between 0.001eV and 0.025eV shows much resonance structure. The first resonance, shown by the dip near 0.002eV is an n=24, v=0 Rydberg state having as its core the $^2\Pi_{3/2g}$ ion. This series of v=0 levels has its limit at 0.025eV at the v=0 level of $^2\Pi_{3/2g}$. These resonances appear as dips because the $^1\Sigma_u^+$ dissociative state is only weakly connected to these levels due to a poor Franck-Condon factor. The peak near 0.03eV is due to a Rydberg n=9,v=1 state with the lower $^2\Pi_{1/2g}$ core. The next peak near 0.06eV is due to the n=9, v=1 Rydberg level with the $^2\Pi_{3/2g}$ core. The peak at 0.07eV is due to n=10, v=1 with the $^2\Pi_{1/2g}$ core. These three resonances all have peaks because both $f^1\Sigma_u^+$ and $B^3\Sigma_u^-$ have a high Franck-Condon factor with these levels leading to an increase in the O(^{1}S) quantum yield at the resonance positions. The calculated rate constant at 300K electron temperature for DR of the $X^2\Pi_{1/2g}$ v=0 level is 0.39(+0.31 -0.19) x 10^{-8} cm^3/sec. For the upper v=0, $X^2\Pi_{3/2g}$ level the DR rate constant is 0.16(+0.16 -0.13) x 10^{-8}cm^3/sec also at 300K electron temperature. The calculated quantum yield from the v=0, $X^2\Pi_{1/2g}$ level is 0.020(+0.015 -0.010) at 300K electron temperature and falls within the range of quantum yields deduced from laboratory and rocket experiments.

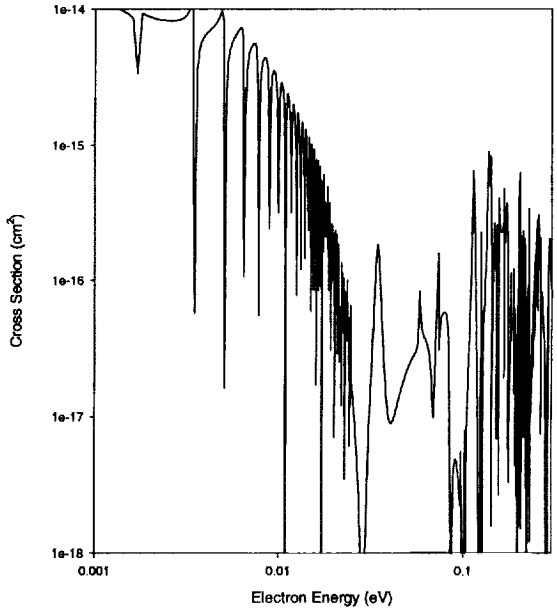

Figure 1. DR cross section for O(^{1}S) from O_2^+.

B. References

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C. Publications Acknowledging NASA Support

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